

PROPERTIES OF BASE FLUIDS FOR ENVIRONMENTALLY ADAPTED LUBRICANTS

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SUMMARY

Five different fluids, two hydrocarbons and three ester based fluids, suitable for use as base oils for environmentally adapted lubricants have been investigated. The fluids are environmentally adapted to different degree, and have a well-defined molecular structure. The tested properties relate to the macroscopic / molecular behaviour and included: viscosity-temperature-pressure-effects, $\eta(p,T)$, thermal conductivity, $\lambda(p,T)$ and heat capacity per unit volume, $\rho_p(p,T)$.

Keywords: lubrication, environmentally adapted lubricants, EAL, viscosity, pressure-viscosity, thermal conductivity

1 INTRODUCTION

Future lubricants are expected to be environmentally adapted whilst maintaining good performance characteristics. The properties of different base fluids vary widely and it is important to understand the effects of these on the performance of a lubricant in the full film and mixed lubrication regimes. To be able to select an appropriate lubricant quickly and efficiently, the properties of the base fluid have to be considered. Base oil properties can be divided into a number of different groups: Lubrication, physical, molecular, and environmental. In this investigation lubrication properties have not been included. Physical properties are those related to transport and state. To be able to perform EHL analyses, the effects of pressure on different properties must be known. It would be of great value if the coupling between physical properties and molecular properties were better understood. In the present work, measurements of some of the most important physical properties have been carried out on five synthetic and pure base fluids. This allows correlation between the physical and rheological properties against the molecular structure.

2 FLUIDS

Five different fluids have been investigated (see Table 1 and Fig.1). All the fluids have well-defined molecular structure, are environmentally acceptable to different degrees, and are potential base fluids, or model compounds for base fluids.

Non of the base fluids contain additives. Bis (2-ethyl hexyl) sebacate was chosen as a reference or calibration fluid for the viscosity measurements, since its viscosity-pressure relationship is well known [1], [2]. The sebacate is a synthetic diester and is available in a highly pure form. Fluids B (synthetic) and C (Squalene, a natural product) are pure hydrocarbons with different molecular weights and structures. Fluids D and E are

synthetic tri-esters, both based on the alcohol trimethylol propane (TMP), esterified with fatty acids of natural origin with different chain lengths and saturation/unsaturation patterns.

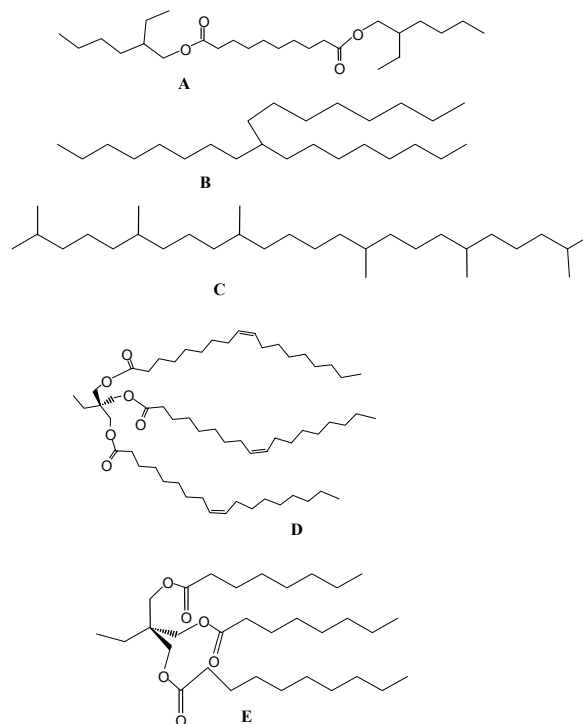


Figure 1. Base fluid structure A-E

#	Fluid	η_{40} [mPas]	M- formula
A	Bis (2-ethyl hexyl) sebacate	10.08	$C_{26}H_{50}O_4$
B	Trioctyl methane	6.6	$C_{25}H_{52}$
C	2,6,10,15,19,23-Hexamethyltetracosane	15.6	$C_{30}H_{62}$
D	TMP Oleate	50	$C_{60}H_{110}O_6$
E	TMP C8/C10	19	$C_{32}H_{60}O_6$

Table 1 The investigated base fluids

3 EXPERIMENTAL METHODS

The fluid characteristics that were determined included, viscosity-temperature-pressure-effects, $\mu(p, T)$, thermal conductivity $\lambda(p, T)$, heat capacity per unit volume, $\rho c_p(p, T)$, density, different molecular parameters and environmental properties.

3.1 High pressure viscosity measurements

To determine the pressure-viscosity relationship at low shear stress, a high pressure Couette rheometer was used [3]. This apparatus consists of a rotational cylindrical viscometer, with a radial clearance of 0.1 mm, which is placed inside a pressure vessel. The pressure can be raised to 500 MPa but 400 MPa is a more normal working pressure. A heater element, which is controlled by an electronic regulator, is warped around the vessel and allows the test temperature to be raised to 80 °C. The shear ratio range of the rheometer is from 0.5 to 20000 s⁻¹, but is limited by the maximum shear stress. The apparatus was calibrated using fluid A, which was used as a reference for the other measurements [1-2]. The temperature- pressure- and viscosity data $\eta(p,T)$ were parameterized against the Roelands pressure-viscosity equation [4]:

$$\eta(p, T) = \eta_0(T) e^{(\ln(\eta_0(T))+9.67)(-1+(1+5.1 \times 10^{-9} p)^{Z(T)})} \quad (1)$$

This relationship is a good empirical model for the pressure range covered in this investigation. It should not, however, be used to extrapolate data to higher pressures [1]. The viscosity at ambient pressure $\eta_0(T)$ can be obtained from:

$$\log(\log(\eta_0 + 4.2)) = -S_0 \log\left(1 + \frac{T}{135}\right) + \log G_0 \quad (2)$$

The parameter $Z(T)$ was obtained from:

$$Z(T) = D_z + C_z \log\left(1 + \frac{T}{135}\right) \quad (3)$$

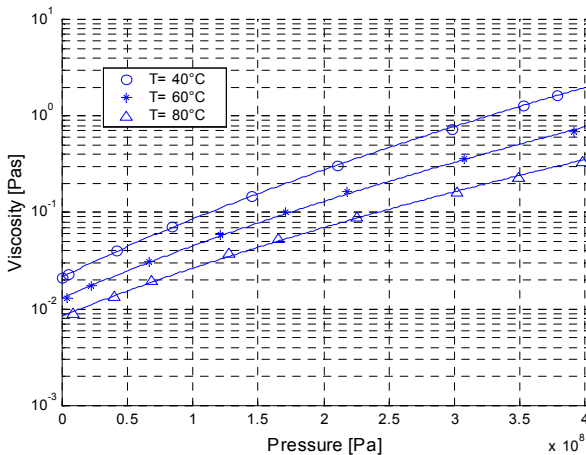


Figure 2. Viscosity data and curve-fit results for Roelands equation (fluid E)

Roelands equation describes a lubricant's pressure-temperature- and viscosity relationship with four coefficients: S_0 , G_0 , D_z and C_z . A shear stress of 100 Pa was chosen, with the shear ratio being adjusted to

achieve the desired shear stress. The tests were carried out isothermally at three different temperatures, 40, 60 and 80 °C. At each temperature the viscosity was measured at several different pressure levels uniformly distributed from about 1 MPa to 400 MPa, see Fig. 2.

3.1.1 The use of Roelands coefficients

If the coefficients in Roelands equation for a given lubricant are known, it is possible to calculate the viscosity for any temperature and pressure within the limits of the measurement range. It is thus possible to calculate both the pressure-viscosity coefficient, (α) and the temperature- viscosity coefficient, (β) for any pressure and temperature. The α value is defined from the Barus expression:

$$\eta = \eta_0 e^{\alpha p} \quad (4)$$

The value of α can be obtained from equation (1) as

$$\alpha(p, T) = \frac{1}{p} (\ln(\eta_0(T)) + 9.67) \times (-1 + (1 + 5.1 \times 10^{-9} p)^{Z(T)}) \quad (5)$$

The value of β is defined as

$$\eta(T) = \eta_{40} e^{-\beta(T-T_0)} \quad (6)$$

where η_{40} is the dynamic viscosity at 40 °C and T_0 is 40 °C.

3.2 Thermal conductivity and heat capacity

The transient hot wire method [5] was used to measure heat capacity per unit volume, $\rho c_p(p, T)$, and thermal conductivity, $\lambda(p, T)$, simultaneously. The technique requires that the tested fluid is placed in a PTFE test cell in which a Nickel (Ni) wire, approximately 40 mm long with a diameter of 0.1 mm is located. A 1.4 s constant power pulse is applied to the wire and by measuring the wire's resistance against time, its temperature rise can be determined. (These data can then be fitted to a theoretical expression from which heat capacity per unit volume and thermal conductivity can be determined.) An analytical solution for the temperature rise was fitted to the data points, thereby yielding λ and ρc_p . The accuracy is estimated to ca. $\pm 2\%$ for λ and ca. $\pm 5\%$ for ρc_p .

By placing the test cell in a pressure vessel the pressure could be raised up to 1 GPa. An electronic regulator was used to control the rate of pressure increase with the rate up to 1 GPa being set to 3.3 MPa/minute; necessary to avoid uncontrolled temperature rise during pressurization. The operating temperature of the cell could be raised to 80 °C by heating the pressure vessel. The temperature is measured using a type K thermocouple and is controlled by an electronic regulator. Data were collected every 150 s and stored in a file.

3.3 Density measurements

The density-temperature relationship for the tested oils was measured at atmospheric pressure with a standard pycnometer. The pycnometer was first weighed empty

then filled with oil and placed in an electric oven for several hours. When the oil had reached the test temperature the pycnometer was weighed again and the density calculated. The density was determined at 40, 60, 80 and 100°C. The result was parameterized in to a density temperature relationship:

$$\rho(T) = \rho_{15} + \frac{d\rho}{dT}(T - 15) \quad (7)$$

3.4 Viscosity- temperature at ambient pressure

To be able to calculate the Viscosity Index, and to obtain additional information about the viscosity-temperature relationship, $\eta(T)$, a test in a Bohlin CS Rotational viscometer was carried out. Tests were performed at constant temperature and with a shear stress range from 10 to 1000 s⁻¹. The lubricants were tested at 40, 60 and 80°C.

3.5 Molecular parameters

The following molecular parameters were determined; non-polarity index, molecular mass and the number of carboxylate groups. The non-polarity index (NPI) is defined as [6]:

$$NPI = \frac{\text{Total number of C atoms} \times \text{Molecular weight}}{\text{Number of carboxylic groups} \times 100} \quad (8)$$

The two pure hydrocarbons have no carboxylate groups and the synthetic esters studied have either two or three, see Table 2.

#	A	B	C	D	E
NPI	55	~300	~300	186	72
Mw	426.37	352.41	422.49	926.83	540.44
COOR	2	0	0	3	3

Table 2. Molecular properties

4 RESULTS

4.1 High pressure viscosity

The parameters obtained from curve fitting Roelands equation are presented in Table 3.

#	S ₀	G ₀	D _z	C _z
A	0.8563	2.8898	-0.0086	0.5368
B	0.7455	2.543	0.211	0.5834
C	1.0133	3.3433	-0.0521	0.6187
D	0.7338	3.5151	0.1889	0.4865
E	0.8495	3.1578	0.0713	0.5246

Table 3. Roelands coefficients for the lubricants

The α value is obtained from Equation 5, see Table 4.

#	$\alpha@20^\circ\text{C}$ p=0 MPa	$\alpha@20^\circ\text{C}$ p=400MPa	$\alpha@80^\circ\text{C}$ p=0 MPa	$\alpha@80^\circ\text{C}$ p=400MPa
A	1.22*10 ⁻⁸	1.20*10 ⁻⁸	1.22*10 ⁻⁸	0.91*10 ⁻⁸
B	1.61*10 ⁻⁸	1.24*10 ⁻⁸	1.32*10 ⁻⁸	1.04*10 ⁻⁸
C	2.10*10 ⁻⁸	1.64*10 ⁻⁸	1.49*10 ⁻⁸	1.16*10 ⁻⁸
D	1.86*10 ⁻⁸	1.35*10 ⁻⁸	1.54*10 ⁻⁸	1.14*10 ⁻⁸
E	1.74*10 ⁻⁸	1.29*10 ⁻⁸	1.35*10 ⁻⁸	1.00*10 ⁻⁸

Table 4. α values

The β value was calculated from Equation 6, see Table 5 for some examples.

#	β , P=0 MPa	β , P=400 MPa
A	0.0225	0.0391
B	0.0235	0.0293
C	0.0275	0.0561
D	0.0287	0.0364
E	0.0270	0.0406

Table 5. β values

4.2 Thermodynamical properties

The thermal conductivity and heat capacity per unit volume at ambient pressure are presented in Table 6.

#	λ_0 [W/m °C]	$\rho C_p 0$ [J/m ³ °C]
A	0.143	1.81*10 ⁶
B	0.153	1.76*10 ⁶
C	0.123	1.68*10 ⁶
D	0.164	1.84*10 ⁶
E	0.148	1.86*10 ⁶

Table 6. Thermodynamic data

The plotted raw data for the thermal conductivity and heat capacity per unit volume up to 1 GPa are shown in Figs 3 and 4. As can be seen in Fig. 4, fluid B is the only fluid with a transition in the investigated pressure range. This transition is due to crystallization, and is seen as a jump in the thermal conductivity curve.

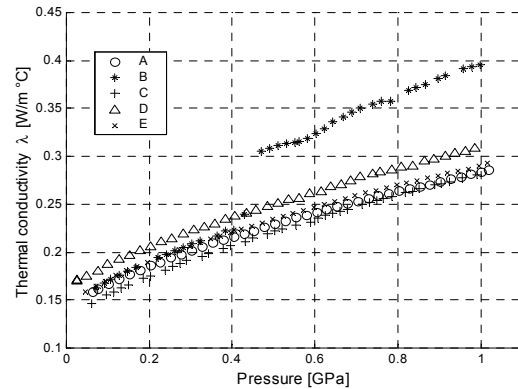


Figure 3. Thermal conductivity as a function of pressure at 20 °C.

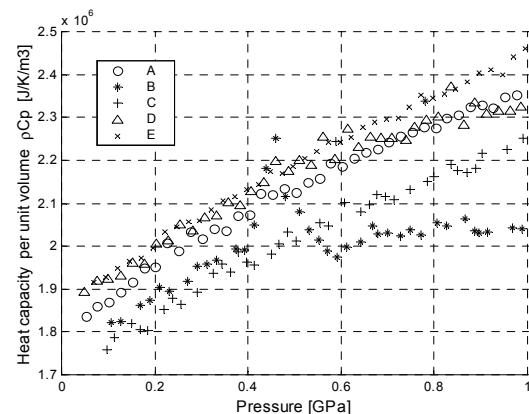


Figure 4. Heat capacity per unit volume as a function of pressure at 20 °C.

4.3 Density measurements

The density parameters were calculated from the pycnometer measurements, see Table 7. All investigated fluids have a linear density variation with temperature.

#	ρ 15 °C [kg/m ³]	dp/dT
A	917	-0,697
B	804	-0,603
C	811	-0,619
D	920	-0,631
E	945	-0,6093

Table 7. Density data

4.4 Environmental properties

There are many ways to characterize a fluid from an environmental perspective. In this paper biodegradability and the amount of renewable raw material have been considered. Biodegradability measures were based on OECD 301 B/F, see Table 8. In the synthetic esters D and E, the polyol alcohol is a non-renewable raw material, whilst the fatty acids are. In the calculation, the ester bond is “broken in half”, and one oxygen atom per ester group is assigned to the “alcohol part”. The fatty acid fragment begins with the carbonyl fragment (carbon-oxygen double bond).

#	A	B	C	D	E
Renewable [%]	39	0	100	85,5	77,5
OECD 301 B/F	80 ¹	10 ¹	50 ²	81	75

Table 8. Biodegradability and relative amount of renewable raw material.

5 DISCUSSION

The α - value varies relatively much. It is low for fluid A and it is not influenced very much by pressure and temperature. For fluid C it is high at ambient pressure and is significantly reduced at higher pressures and temperatures. The β - value is low for A and B and somewhat higher for C, D and E at ambient pressure but at higher pressure there is a greater variation for some of the fluids. All three esters have relatively high thermal conductivity (especially C and D) and heat capacity per unit volume (Table 6). This is probably related to the presence of the ester groups, rather than to any difference caused by the molecular structure.

The Non Polarity Index, is a rather useful tool for classifying fluid- surface interaction and solubility of additives. The NPI is listed in this study for the sake of comparison, and will be used in future work.

The EHL friction coefficient γ is shown in Table 9 [8]. Fluid C has, for example, almost twice as high γ - value as D, and use of D instead of C will thus reduce the EHL friction to 50%.

#	A	B	C	D	E
$\gamma@$ 2GPa	0.047	0.038	0.056	0.031	0.042

Table 9 EHL friction coefficients

¹ Estimated biodegradability

² Source: [8], [9]

The influence of the different base oil properties on lubrication parameters are presented in Table 10 [7]. It shows how different properties should be optimized. “High” means that a high value is preferable, “Low” means low value is preferable and “H/L” means its influence is ambiguous. Fluid C has the highest α - value and its molecular structure is representative for an iso-paraffinic hydrocarbon. A high α - value is beneficial for film build-up, but results in higher friction.

Parameter	η_0	α	β	$\rho_{cp}0$	λ_0
Film thickness	High	High	Low	High	High
Friction	Low	Low	H/L	?	H/L
Pressure peaks	H/L	Low	?	?	?

Table 10. Influence of different properties on lubrication parameters

It is too early to draw any general conclusions about the coupling between molecular parameters and the physical properties, but future investigations will give further understanding of the important mechanisms.

6 ACKNOWLEDGEMENTS

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